

Investigation of Mixed Oxide Catalysts for NO Oxidation

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Pacific Northwest National Lab
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Project ID #
ACE078

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Overview

► Timeline

- Start – Oct 2011
- Finish – Sept 2014
- 36-month CRADA

► Budget

- Total project funding
 - DOE: \$450k (\$150k/year)
 - Matched 50/50 by GM per CRADA agreement
- Funding authorized to-date: \$450k

► Barriers

- Reduce or optimize PGM usage as “critical materials” in emission control devices
- Development of low-temperature oxidation catalysts
- Better understanding of active sites and structure requirements in catalysts
- Design and modeling of catalyst functions and structures

► Partner

- General Motors
- GM’s university partner in China (Tianjin University)

Motivation and relevance

- ▶ Higher efficiency engines often implies lower exhaust temperature, requiring better low-temp catalysis to meet emission regulations by inexpensive and reliable NO_x emission control

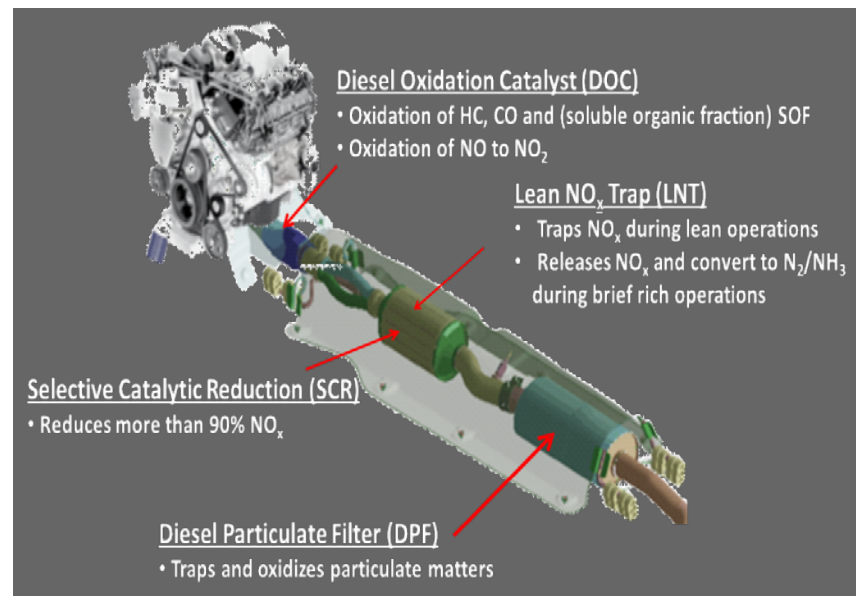
- NO to NO₂ required for NO_x storage on LNT
- NO₂ may assist passive regeneration of soot in DPF

- ▶ Pt is the most active catalyst

- Pt commodity pricing is still high and volatile, although the rate of increase is leveling off

- ▶ Thrifting or replacement of Pt in DOC and LNT catalysts desired for:

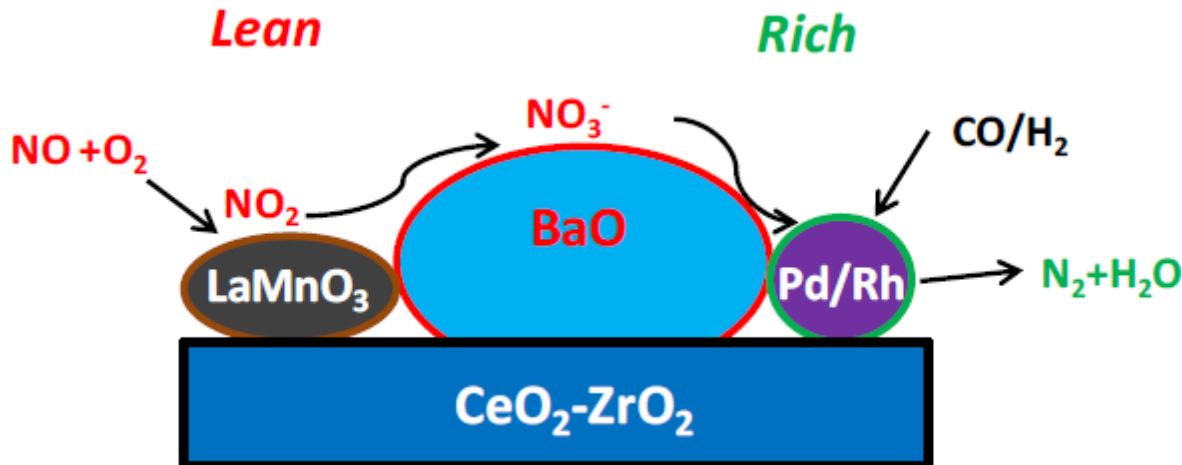
- supply-chain stability
- cost reduction as an enabler to advanced aftertreatment and combustion technologies
- alternative technologies for oxidation reactions



Objectives

This CRADA project aims to *develop and demonstrate a substitutive option for Pt oxidation function using mixed-metal oxide structures.*

- ▶ Improve the understanding of the nature and structure of active sites for mixed metal oxide catalysts intended for NO oxidation
- ▶ Study of synthetic method and composition on resulting structure and on effectiveness of NO oxidation



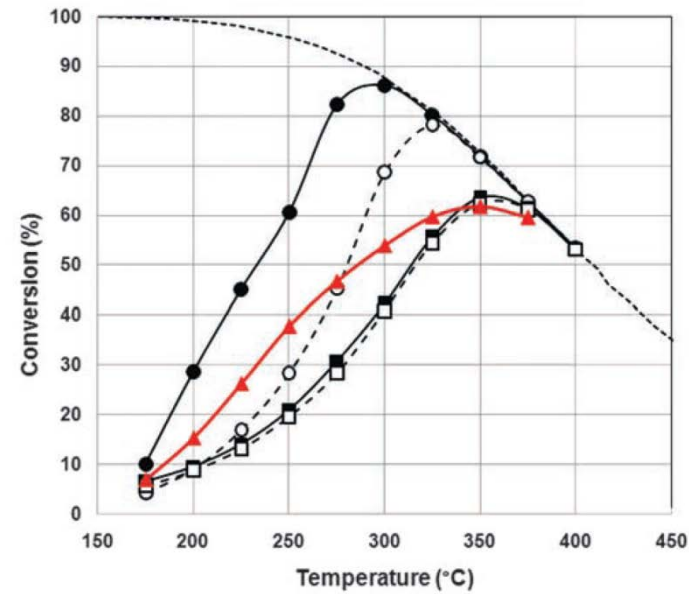
- Typical LNT catalyst structure (left)

Partnership with GM – CRADA

Gongshin Qi and Wei Li

- ▶ Based on research reported by GM (Science 327 (2010) 1624)
 - CRADA initiated for PNNL assistance leveraging surface science and catalysis capabilities
 - Analytical assessment and computational model
- ▶ Scope split, but coordinated between GM and PNNL
 - GM - Catalyst formulation, aging and testing
 - PNNL - Characterize structure and active sites, along with alternative synthesis processes and assessment of the effect on performance

Fig. 1. NO oxidation activities for LaCoO_3 (\circ), $\text{La}_{0.9}\text{Sr}_{0.1}\text{CoO}_3$ (\bullet), LaMnO_3 (\square), $\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$ (\blacksquare), and commercial DOC (\blacktriangle) at a gas hourly space velocity of $30,000 \text{ hour}^{-1}$; 400 parts per million (ppm) of NO and 8% of O_2 in a balance of N_2 .

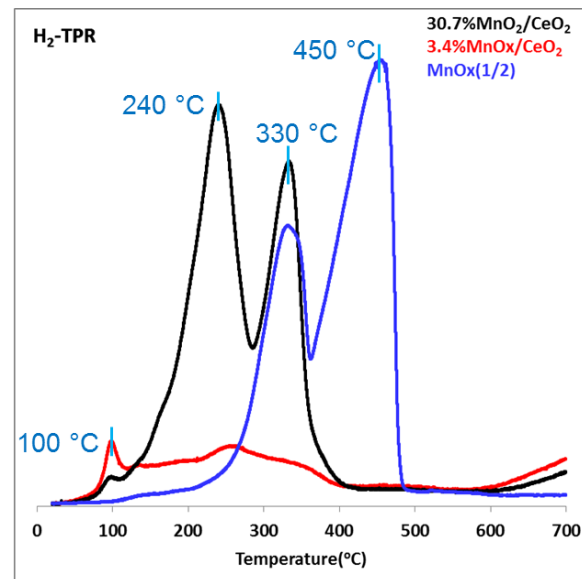
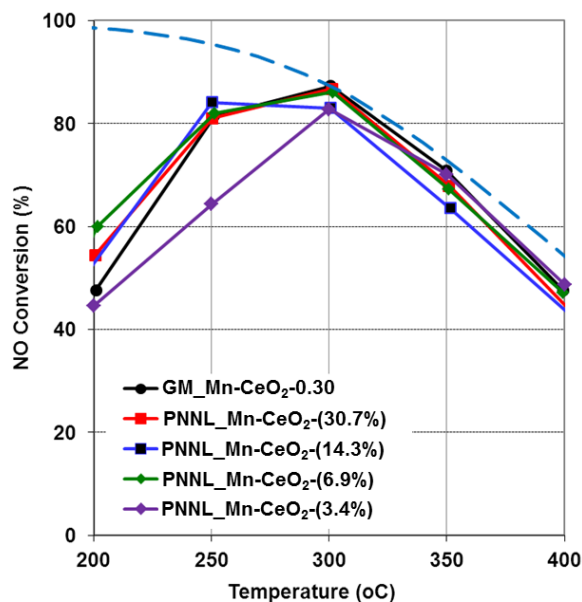
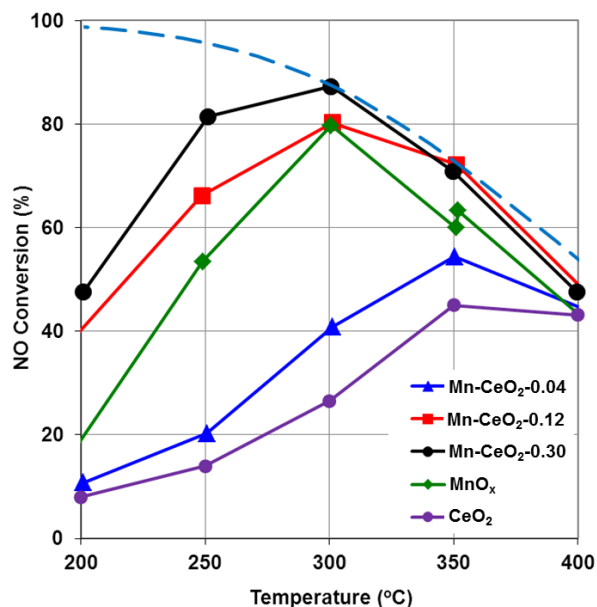


Science 327 (2010) 1624

MnO_x-CeO₂ interaction (Project summary for first two years)

Technical Progress

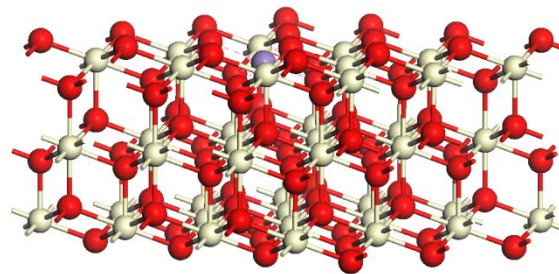
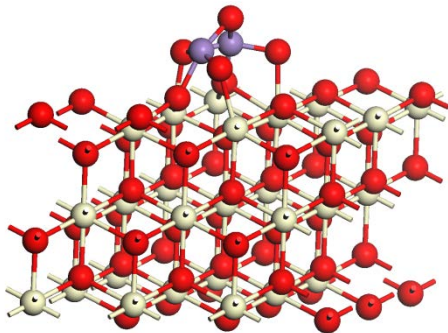
Previously presented



- ▶ MnO_x/CeO₂ is more active than MnO_x and CeO₂.
- ▶ MnO_x/CeO₂ is more reducible than bulk MnO₂.
- ▶ High activity of catalysts prepared by incipient wetness suggest that Mn doping in CeO₂ is not necessary.
- ▶ FTIR showed lower NO binding energy and higher activity for NO₃⁻ decomposition on MnO_x/CeO₂.
- ▶ DFT results suggest that MnO_x(clusters)/CeO₂ is more active than MnO_x and CeO₂ in agreement with activity and IR results.

Critical questions for developing a highly active and stable $\text{MnO}_x\text{-CeO}_2$ NO oxidation catalyst

- ▶ MnO_2 clusters/ CeO_2 or $\text{Mn}_x\text{Ce}_{(1-x)}\text{O}_2$ mixed oxide?



- ▶ Optimum oxidation state for Mn?
 - Effect of $\text{MnO}_x\text{-CeO}_2$ interaction on labile oxygen
- ▶ Stability
 - Effect of aging
 - Sulfur tolerance

Milestones and planned 3rd year tasks

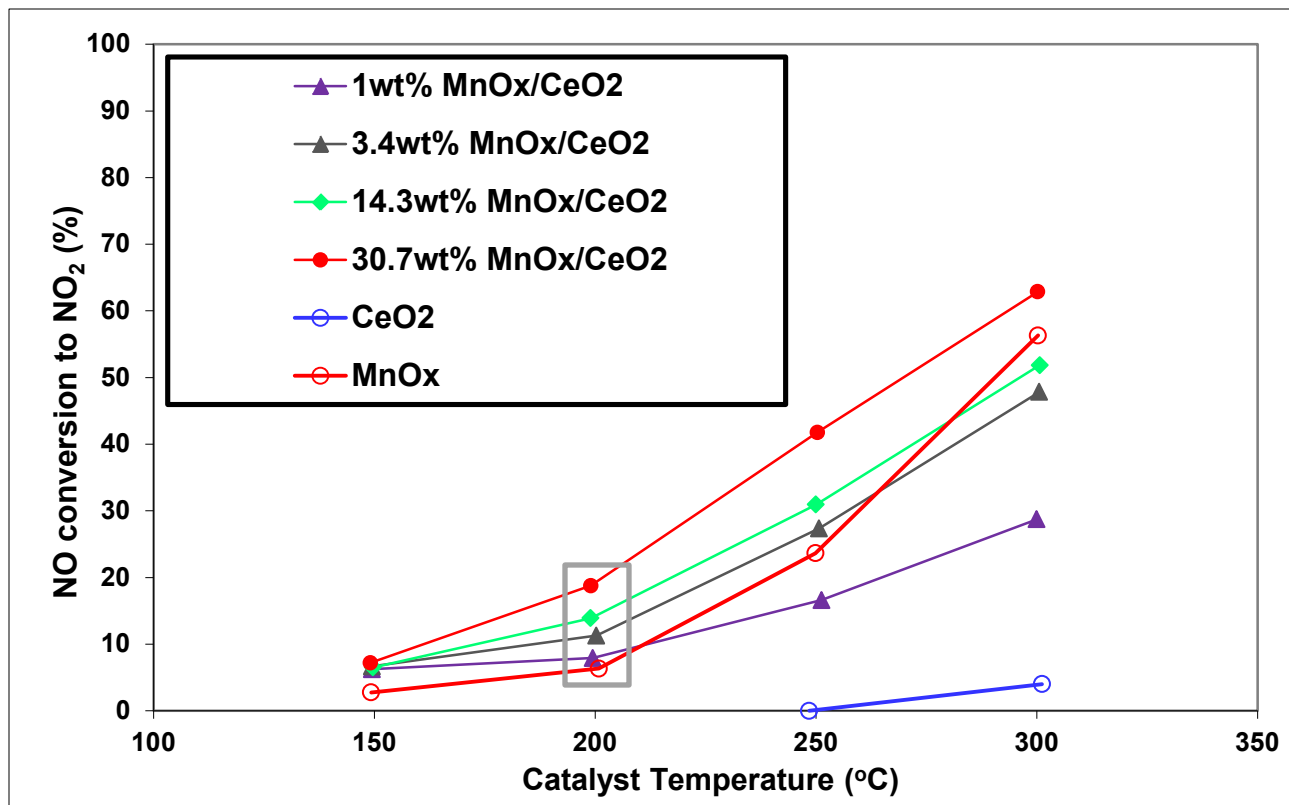
- ▶ Compete catalytic reaction tests to understand the role of NO_x storage capacity
 - Catalyst formulation, aging and sulfur tolerance by GM
 - Alternate synthesis methods
 - Characterize structure and number of active sites
 - Identified mixed metal oxide catalyst compositions and forms that show high activity and stability for NO oxidation.
- ▶ Perform detailed characterization by FTIR
 - Using isotope labeling studies, we demonstrated that the MnO_x-CeO₂ catalyst both decreased the required temperature for NO₂ formation and increased the quantity of labile oxygen needed for NO oxidation.
 - Showed that the most active sites likely consist of small MnO₂ clusters interacting strongly with CeO₂.
 - Mn doping in CeO₂ is not necessary.
- ▶ Complete study of the effects of MnO₂ cluster size on the reaction mechanism by DFT
 - DFT calculations confirmed the active sites identified by XAFS and XPS and the role of MnO_x-CeO₂ interaction in increasing the oxygen mobility.

Approach

- ▶ Prepare and evaluate both fresh and lab-aged catalyst materials to optimize the formulations for DOC and LNT applications

- ▶ Utilize catalysis expertise, state-of-the-art analytical techniques and computational analysis to investigate:
 - Surface and bulk properties of the catalyst materials with respect to changes in composition;
 - XPS, XAFS
 - Interaction between reactants and the potential active sites
 - FTIR, TPD, DFT
 - And help inform more advanced catalyst formulations

Total activity is not proportional to Mn loading



- ▶ A 3.4x increase in Mn loading results in only 2x increase in conversion in the kinetic regime.
- ▶ Activity should be normalized to the Mn sites on the surface
 - Use %Mn from XPS and BET surface area to estimate # Mn surface sites

50mg, 156 sccm (GHSV = 300,000 hr⁻¹)

Gas composition: 200 ppm NO, 10% O₂, 10% water, balance N₂

Normalized activity results at 200 °C show higher intrinsic activity for lower Mn loading

	Fraction monolayer (no 3D structures)	BET surface area (m ² /g)	Surface/Bulk Mn (XPS)	Surface Mn/Ce (XPS)	Reaction rate (mol/Surface mol Mn min)
MnO _x	1	14.7	0.91	-	541
1% MnO _x /CeO ₂	0.046	136	-	-	-* (1772)**
3.4% MnO _x /CeO ₂	0.16	132	1.13	0.2	476* (592)**
14.7% MnO _x /CeO ₂	0.77	115	0.99	0.64	212* (176)**
30.7% MnO _x /CeO ₂	2.2	87	0.93	0.69	348* (240)***

14.3% MnO_x/CeO₂ TEM/EDS confirm fractional MnO_x coverage.

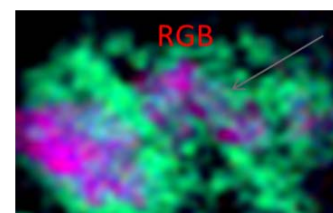
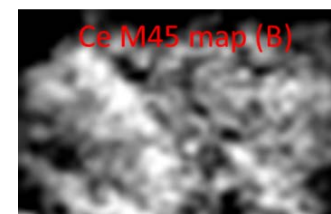
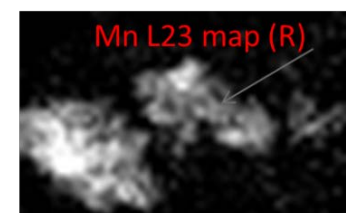
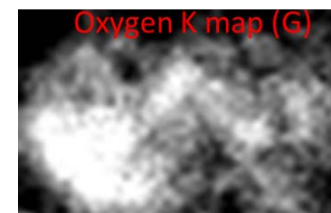
Surface density for MnO₂ and CeO₂ is ~ 11.2 atom/nm²

* using Mn/Ce from XPS

** using fractional coverage (first column)

*** assuming full surface coverage

► Lower Mn loading shows higher intrinsic activity than bulk MnO_x.



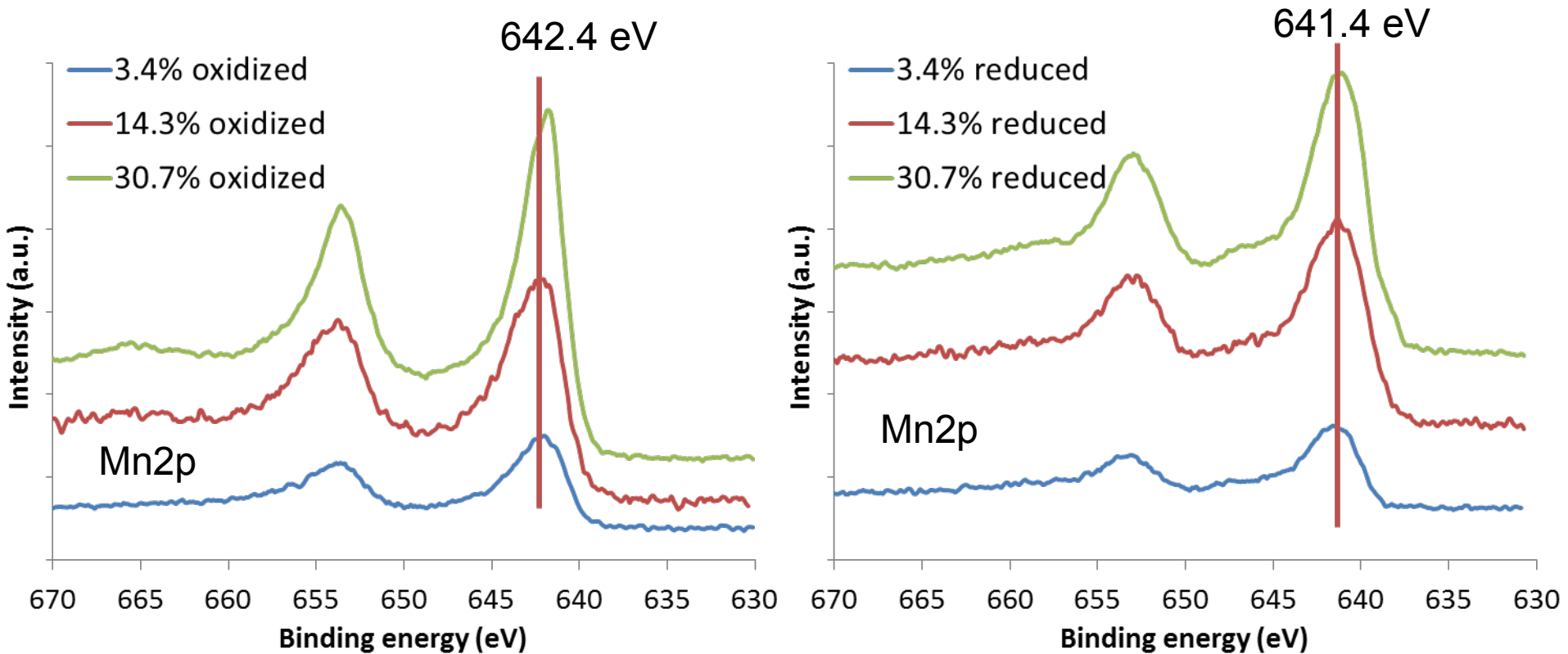
EXAFS results on 3.4%, 30.7% MnO_x/CeO₂ and bulk MnO_x

	Mn–O (Å)	Mn–Mn (Å)
MnO	2.22	3.14
Mn ₂ O ₃	1.89	3.12
MnO ₂	1.86	2.87
Bulk MnO _x	1.90	3.16
3.4% MnO _x /CeO ₂	1.84	2.80
30.7% MnO _x /CeO ₂	1.86	2.86
Mn ₂ O ₄ cluster/CeO ₂	1.93-2.00	2.66
Mn ₂ O ₂ cluster/CeO ₂	1.90-2.1	2.67
Mn doped CeO ₂	2.24-2.28	3.80 (Mn–Ce)
MnO ₂ (110)	1.89-1.90	2.87

DFT

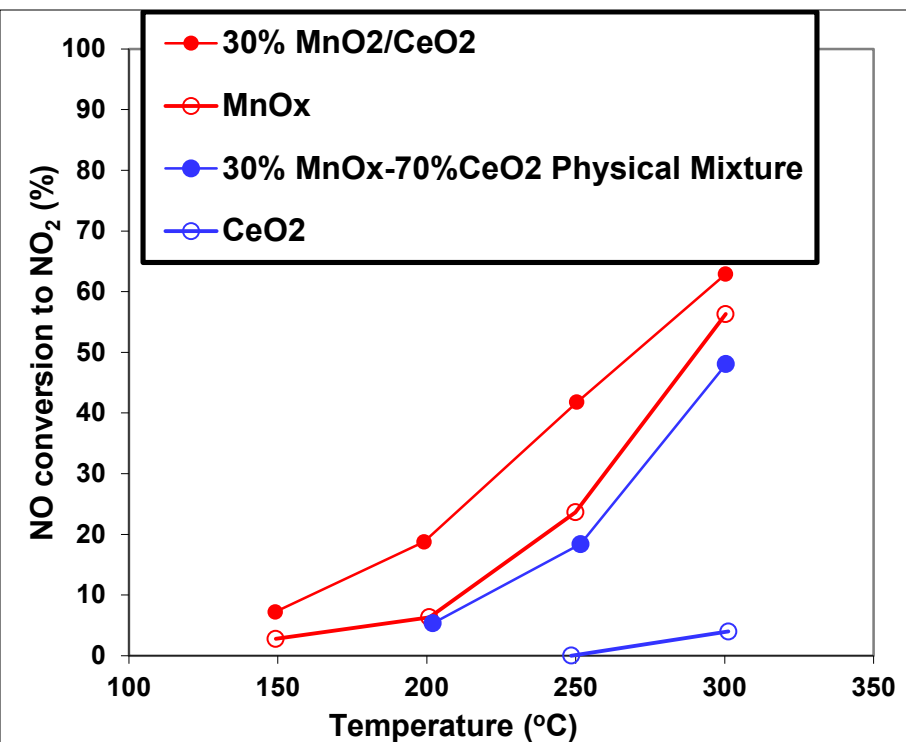
- ▶ Bond distances suggest Mn⁴⁺ (MnO₂) clusters/nanoparticles are formed when MnO_x is supported on CeO₂.
- ▶ Shorter Mn–O bond distance for the 3.4% MnO_x/CeO₂ suggests smaller clusters.

Higher oxidation state detected by XPS on lower Mn loading catalysts



- ▶ Lower Mn loading shows higher Mn oxidation state.
- ▶ From XAFS and XPS, Mn appears to be in close contact with CeO_2 (not in the CeO_2 lattice) and in 4+ oxidation state.

Synergy between MnO_x and CeO_2 is present even in a physical mixture

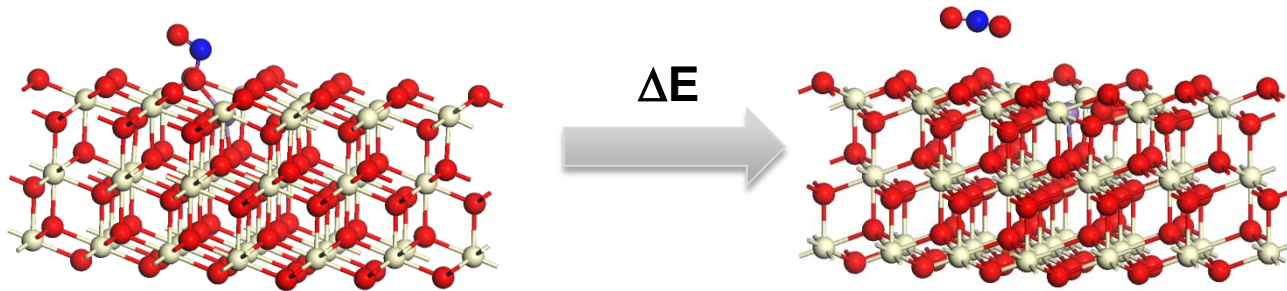
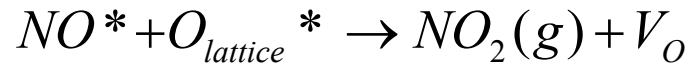


	Reaction rate x10 ⁻³ (mol/m ² /min)	Reaction rate (mol/Surface mol Mn min)
MnO _x	10.1	541
30% MnO _x /CeO ₂ physical mixture	24.8	1332

Calculation assumes negligible CeO_2 activity at 200 °C

- ▶ Physical mixture of MnO_x and CeO_2 shows higher activity than the addition of their individual activities.
- ▶ Results confirm that Mn doping is not necessary.

Effect of Mn doping and MnO₂ clusters on energy barriers for NO oxidation on MnO_x-CeO₂

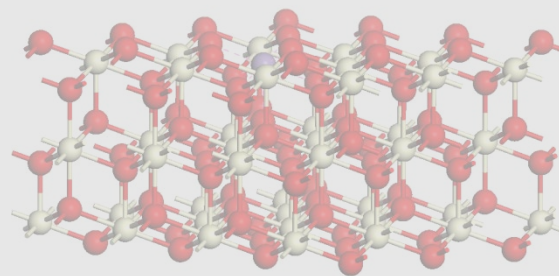
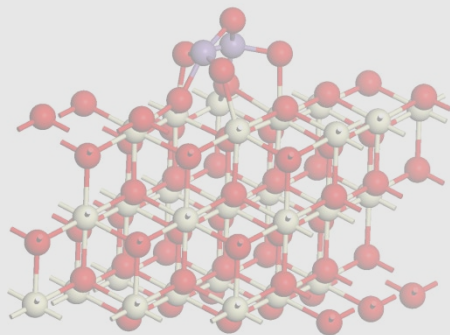


	CeO ₂ (111)	Mn doped CeO ₂ (111)	Mn ₂ O ₄ cluster on CeO ₂ (111)	Mn ₂ O ₄ cluster on CeO ₂ (111)	MnO ₂ (110)
perfect	+2.57	+1.96	-0.01	-0.36	+0.48 eV
defective	+2.38	+2.01	+1.43	+2.79	+0.42

- NO₂ desorption from the surface (creating an O vacancy) is the rate-controlling step in NO oxidation on the CeO₂ based surfaces.
 - For the MnO₂(110) and the CeO₂(111) supported Mn₂O₄ cluster, this step becomes feasible under reaction temperature range while the barrier is too high for the pure and Mn doped CeO₂ surfaces.
 - Mn doping in CeO₂ doesn't significantly lower the barrier
 - MnO₂ clusters/CeO₂ no barrier (exothermic)

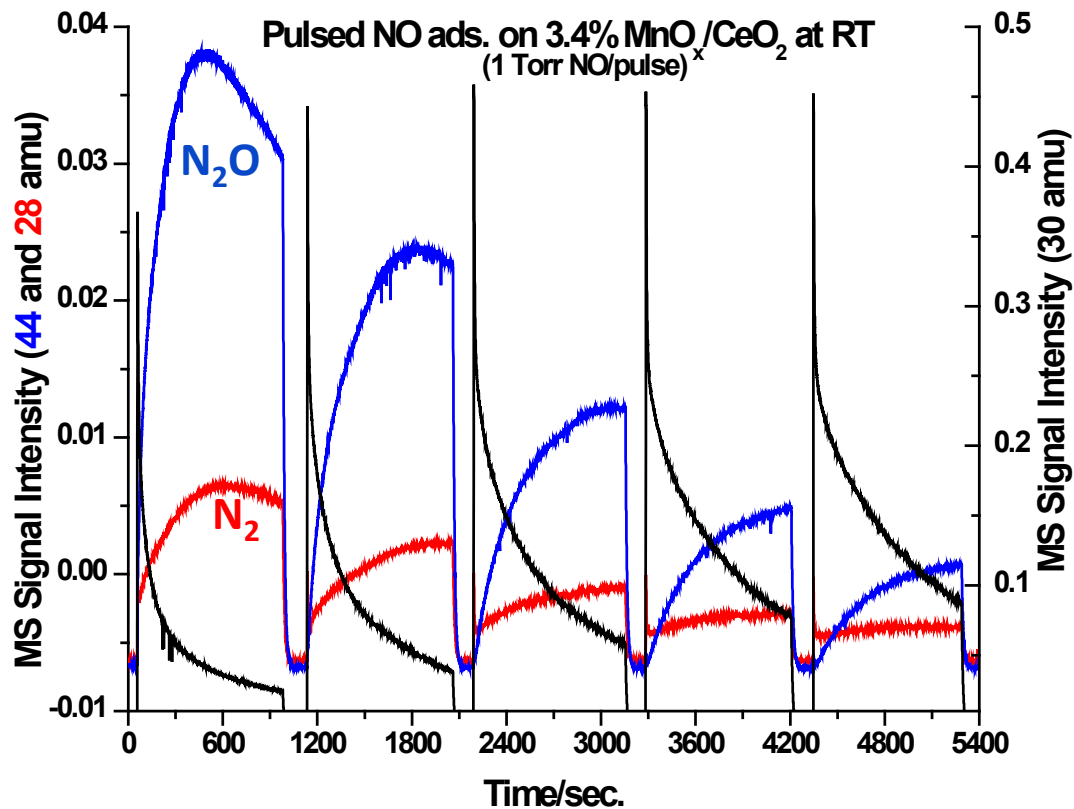
Critical questions for developing a highly active and stable $\text{MnO}_x\text{-CeO}_2$ NO oxidation catalyst

- MnO_2 clusters/ CeO_2 or $\text{Mn}_x\text{Ce}_{(1-x)}\text{O}_2$ mixed oxide?



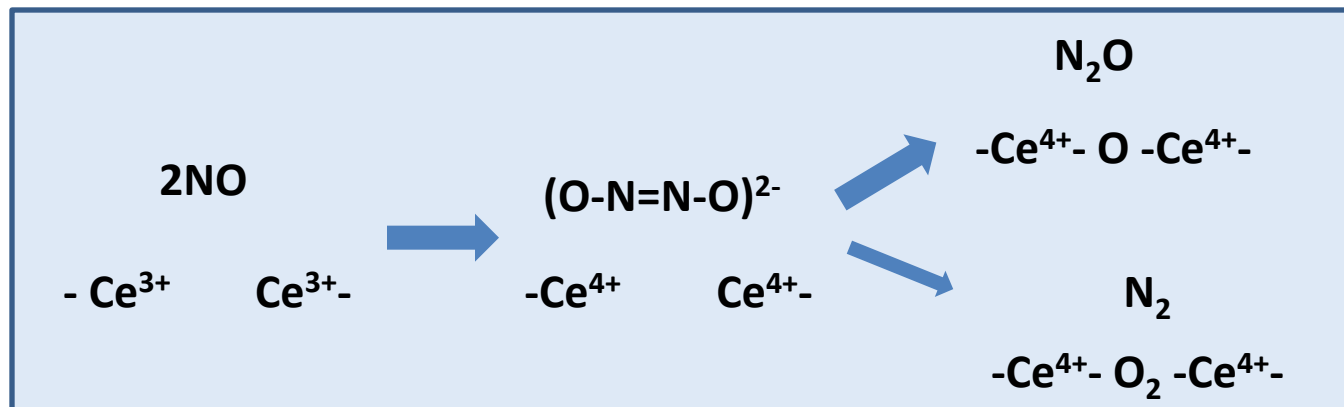
- Optimum oxidation state for Mn?
- Effect of $\text{MnO}_x\text{-CeO}_2$ interaction on labile oxygen
- Stability
- Effect of aging
 - Sulfur tolerance

NO pulses on annealed 3.4% MnO_x/CeO₂ showed reduction of NO

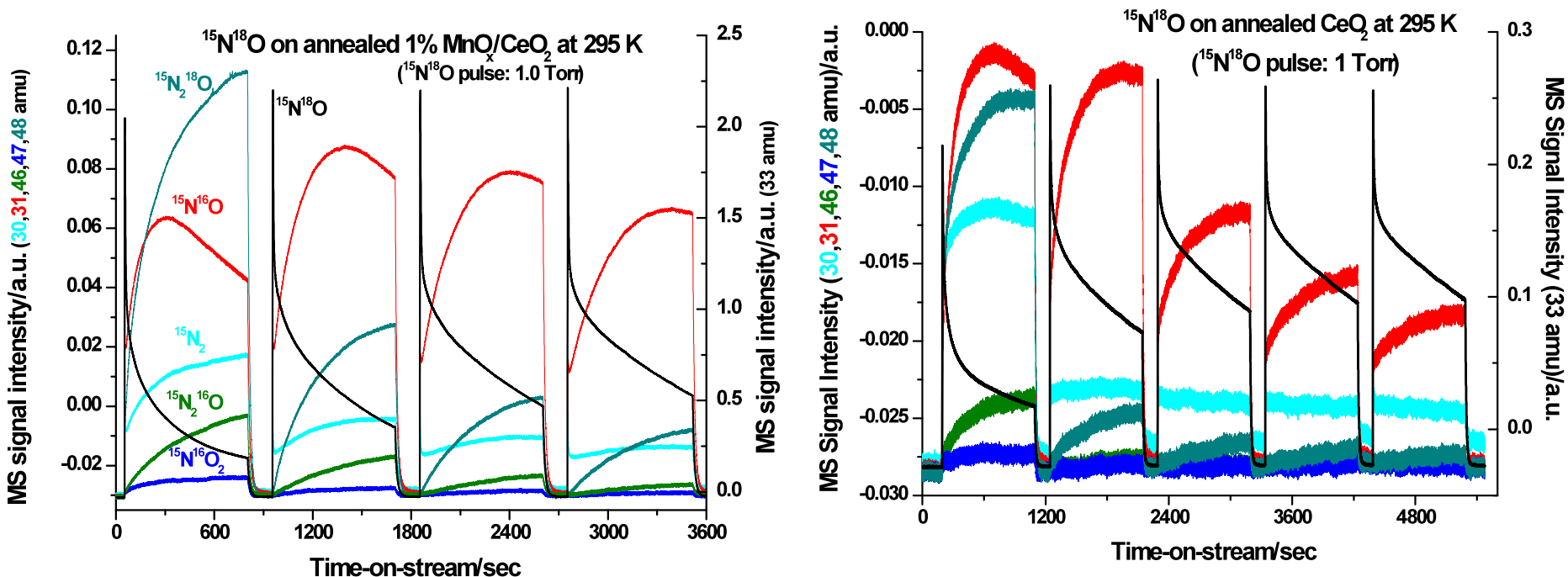


The reduction of NO shows:

1. Presence of O vacancies
2. Possible O scrambling between NO and the surface.



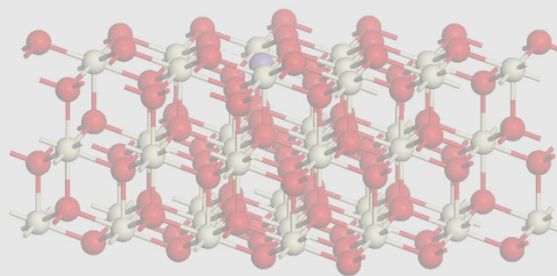
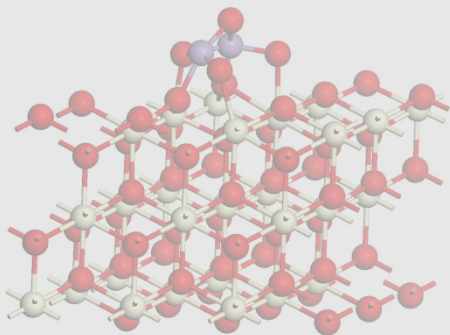
Isotopic labeling studies confirmed higher reducibility due to $\text{MnO}_x\text{-CeO}_2$ interaction



- ▶ More NO reduction is seen on the 1% $\text{MnO}_x/\text{CeO}_2$
 - More O vacancies
- ▶ Faster oxygen scrambling is seen on the 1% $\text{MnO}_x/\text{CeO}_2$
 - O is more labile

Critical questions for developing a highly active and stable $\text{MnO}_x\text{-CeO}_2$ NO oxidation catalyst

- ▶ MnO_2 clusters/ CeO_2 or $\text{Mn}_x\text{Ce}_{(1-x)}\text{O}_2$ mixed oxide?

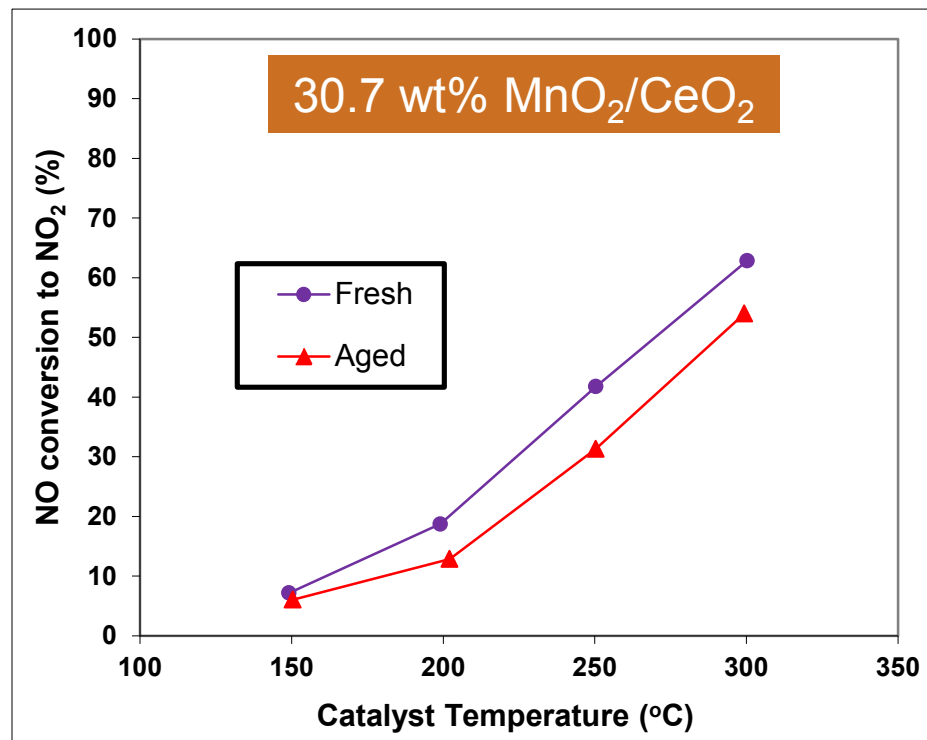
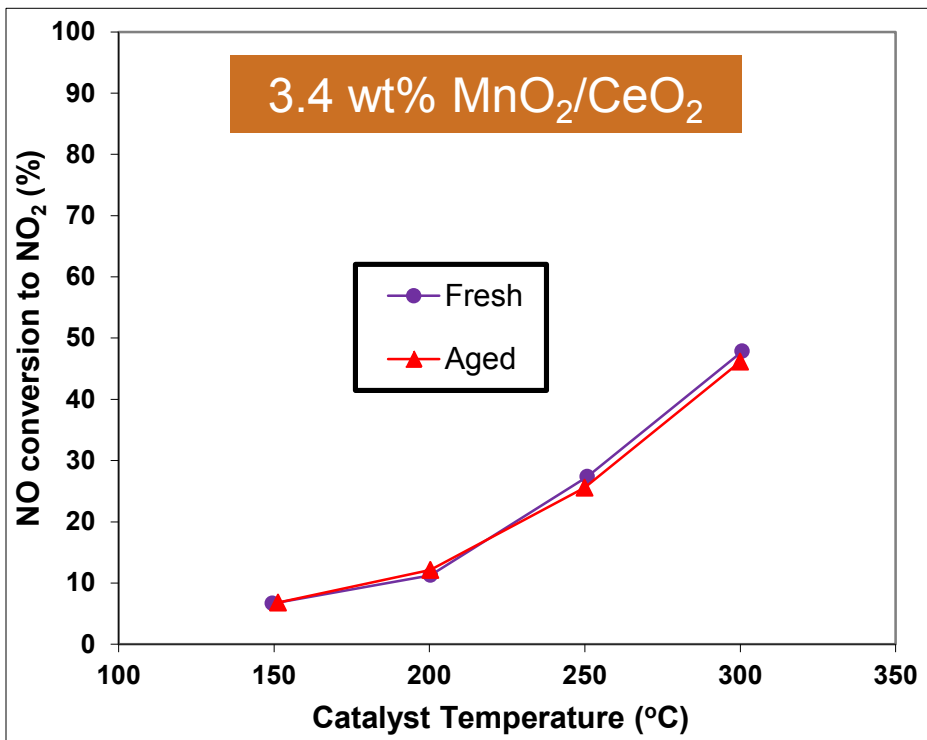


- ▶ Optimum oxidation state for Mn?
 - Effect of $\text{MnO}_x\text{-CeO}_2$ interaction on labile oxygen

- ▶ Stability
 - Effect of aging
 - Sulfur tolerance

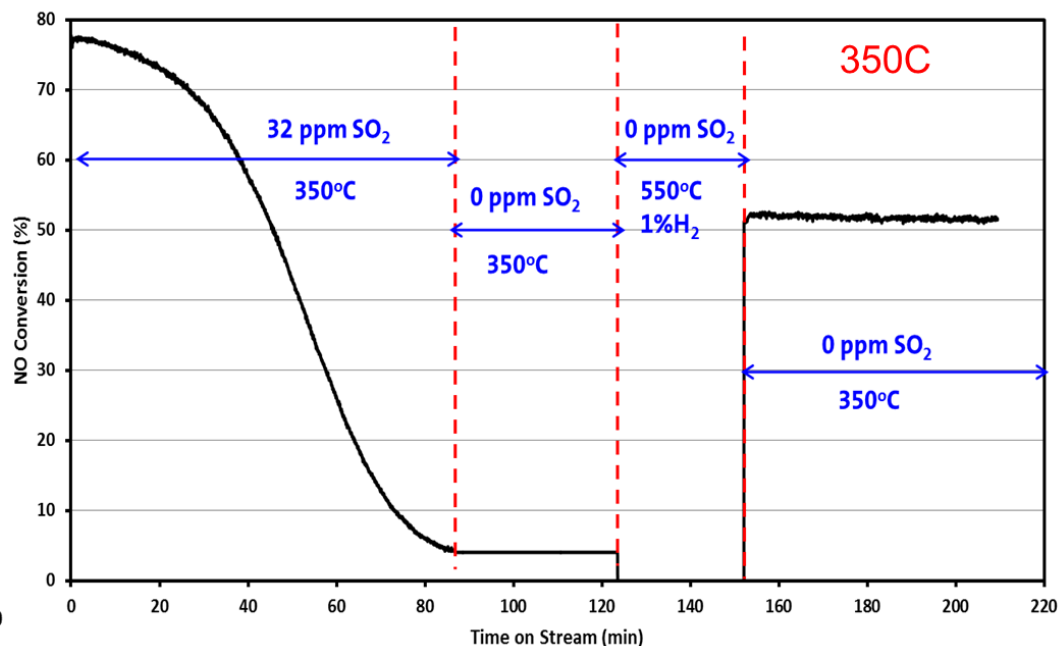
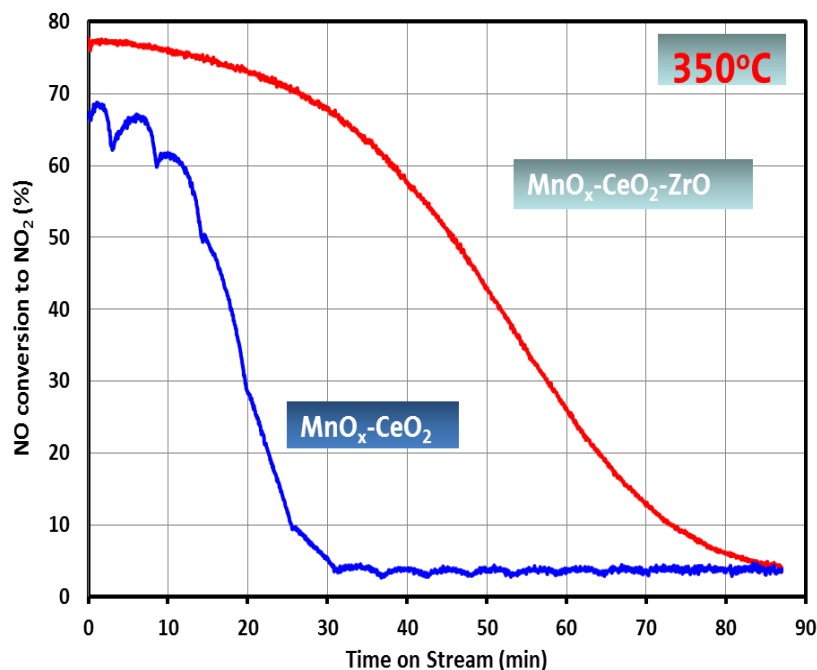
Activity is not significantly affected by aging

Aging was performed at 700 °C in 10% H₂O/air for 1 hour



- ▶ Aging has little effect on catalyst activity
 - Catalysts with higher MnO_x loading are more affected by aging
- ▶ BET surface area measurements show 30-40% loss due to aging

Hydrothermal stability and sulfur tolerance improvement



- ▶ The incorporation of ZrO₂ into MnO_x-CeO₂ mixed oxide resulted in:
 - Increased activity
 - Improved hydrothermal stability
 - Increased sulfur tolerance
- ▶ Sulfur poisoning is not reversible, but ~70% of the conversion can be restored by a rich treatment.
 - More detailed study is currently underway to optimize desulfation treatment.

Response to previous year reviewer comments

- ▶ Durability of Mn catalysts to high temperature and sulfur
 - Addressed by aging studies at GM and PNNL
 - Addressed by sulfur tolerance studies at GM

- ▶ Tianjin University's role
 - Initial DFT calculations were performed at Tianjin University.
 - All calculations were repeated on larger MO_x clusters at PNNL to get better accuracy.

Summary and conclusions

Project progress

- ▶ Catalysts prepared and tested
 - Catalysts prepared by incipient wetness showed highest activity.
- ▶ The active sites were determined by a combination of XPS, XAFS, FTIR and DFT
 - CeO_2 helps stabilize Mn in a higher oxidation state (Mn^{4+})
 - in addition, the Mn is also easier to reduce.
 - NO oxidation, XAFS results and DFT calculations show that Mn doping in the ceria lattice is not necessary.
 - XPS and XAFS suggest that the active sites are small MnO_2 clusters interacting strongly with CeO_2 .
- ▶ The reaction mechanism was investigated by DFT and FTIR.
 - MnO_x - CeO_2 interaction leads to more labile oxygen which significantly lowers the temperature for the conversion of adsorbed nitrites to nitrates.
- ▶ Addition of ZrO_2 improves the hydrothermal stability and tolerance to sulfur
 - Activity can be partially restored after desulfation by a rich treatment

Remaining Barriers and Future Work

- ▶ Goal: Maximize activity and sulfur tolerance of MnO_x - CeO_2 for NO oxidation to enable the noble metal content of DOC and LNT catalysts to be reduced or eliminated.
 - Maximize the number of active sites (and their stability) which are small MnO_2 clusters interacting with CeO_2 (Mn_2O_4 - CeO_2):
 - Investigate the effect of the support on the structure and activity of $\text{MnO}_2/\text{CeO}_2$.
 - Improve sulfur tolerance:
 - Effect of doping with Pd.
 - Effect of regeneration treatment on catalyst activity.

Publications and Presentations

► Publications:

- LR Pederson, JH Kwak, D Mei, DR Herling, GG Muntean, CHF Peden, “Investigation of Mixed Oxide Catalysts for NO Oxidation”, Advanced Combustion Engine Research and Development, FY2012 Progress Report (2012).
- AM Karim, LR Pederson, J Szanyi, Diana Tran JH Kwak, D Mei, GG Muntean, CHF Peden, “Investigation of Mixed Oxide Catalysts for NO Oxidation”, Advanced Combustion Engine Research and Development, FY2013 Progress Report (2013) in press.
- Manuscript on the effect of exchange between NO and oxygen from the lattice is being prepared
- Manuscript on the NO oxidation reaction mechanism and active sites on MnOx-CeO₂ is in preparation.

► Presentations:

- LR Pederson, JH Kwak, D Mei, DR Herling, GG Muntean, CHF Peden, “Investigation of Mixed Oxide Catalysts for NO Oxidation”, Presented by Larry Pederson at the DOE Annual Merit Review, May 2012.
- LR Pederson, AM Karim, JH Kwak, D Mei, GG Muntean, CHF Peden, “Investigation of Mixed Oxide Catalysts for NO Oxidation”, Presented by Larry Pederson at the DOE Annual Merit Review, May 2013.
- Karim et al. “Insights on the active phase and mechanism for NO oxidation on MnOx-CeO₂ mixed oxide”, invited talk at the annual ACS conference in San Francisco, CA, August 10-14 2014.
- Karim et al. “Insights on the active phase and mechanism for NO oxidation on MnOx-CeO₂ mixed oxide”, accepted for oral presentation at the 8th International Conference on Environmental Catalysis in Asheville, North Carolina Aug 24-27 2014.

Technical Back-Up Slides

Catalyst synthesis and BET surface area

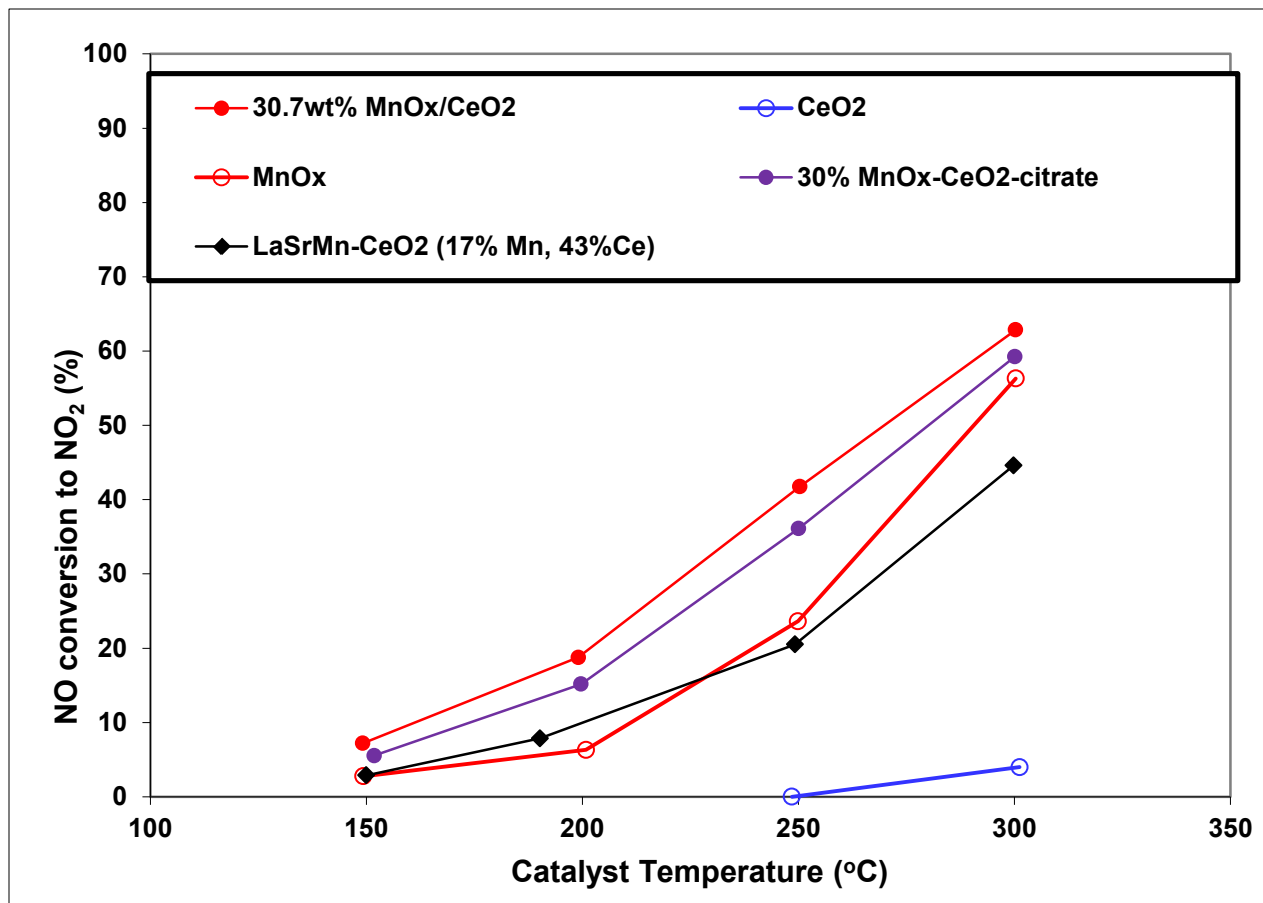
Sample	Surface area(m ² /g)		
	Fresh	After reaction	After aging
HAS-CeO ₂ (GM)	139		
1%MnO _x /CeO ₂	145		106
3.4%MnO _x /CeO ₂	132		71
6.9%MnO _x /CeO ₂	126	124.5	-
14.3%MnO _x /CeO ₂	115	111.5	69
30.7%MnO _x /CeO ₂	87	84.7	51

- ✓ **PNNL catalysts shows high surface area due to the initial high surface area CeO₂.**
- ✓ **Negligible surface area reduction after reaction tests for both GM and PNNL catalysts.**
- ✓ **Aging leads to 30-40% loss in surface area.**

- ▶ **GM: synthesized by co-precipitation method**
 - CeO₂ , MnO_x, Mn-CeO_x (Mn/(Mn+Ce) = 0.04-0.3)

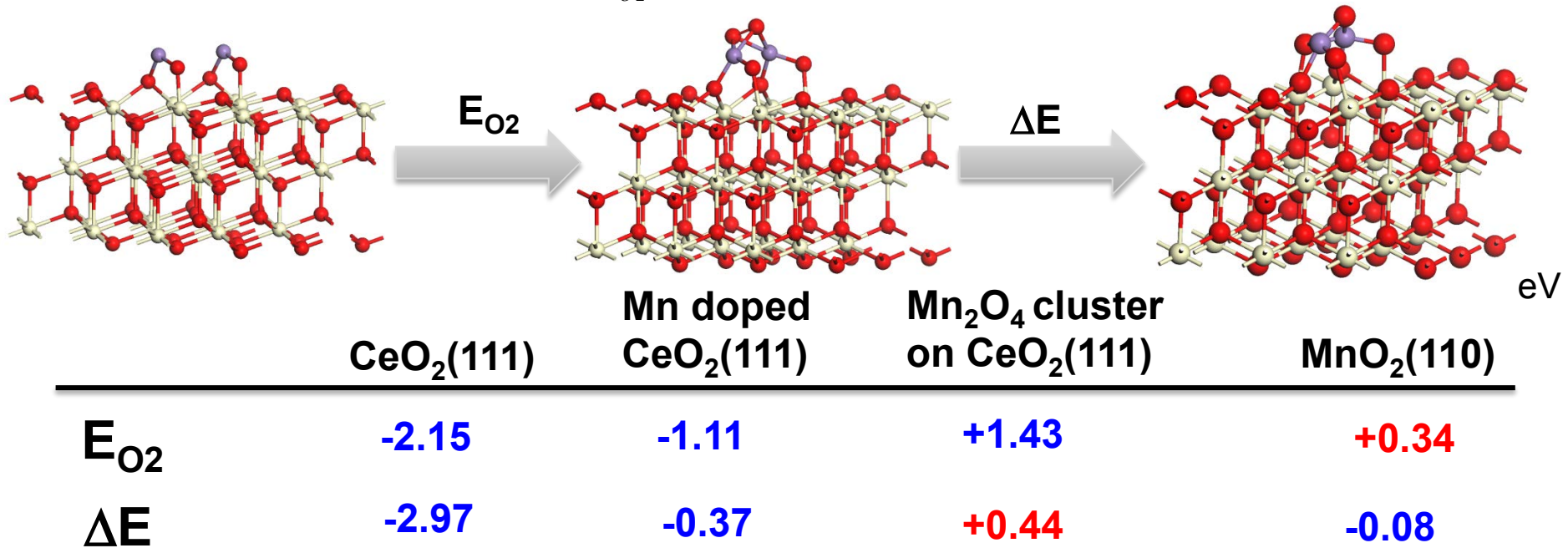
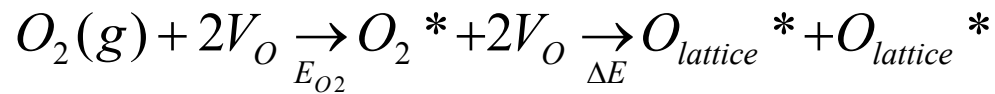
- ▶ **PNNL**
 - Incipient wetness method
 - Support: high surface area CeO₂ (from GM S.A. = ~ 120m²/g)
 - Citrate (co-impregnation)
 - Combustion synthesis
 - MnO_x loading: 3.4, 6.9, 14.3, 30.7 wt%

Effect of synthesis method on catalyst activity



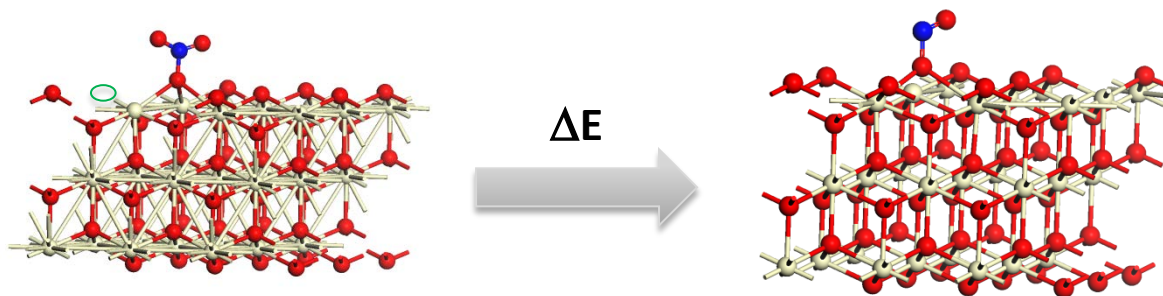
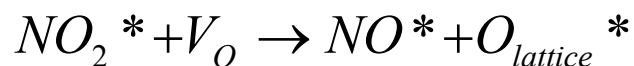
- Co-precipitation (citrate) or combustion methods of catalyst preparation didn't show an advantage over incipient wetness.

Oxygen Activation on Defective Surfaces



- Generally, molecular oxygen adsorption and activation over defective (two defect sites) surfaces are thermodynamically favored.

NO₂ reduction on the defective surfaces



	CeO ₂ (111)	Mn doped CeO ₂ (111)	Mn ₂ O ₄ cluster on CeO ₂ (111)	MnO ₂ (110)
E_{NO_2}	-1.34	-0.81	-0.84 ~ -3.52	-1.31
ΔE	-1.23	-0.22	+0.89 ~ +3.63	+0.83

eV

- ▶ With existing oxygen defects, the adsorbed NO₂ will reduce to NO and O on the CeO_{2-x} and the Mn doped CeO_{2-x} surfaces.
- ▶ It is thermodynamically unfavorable for the adsorbed NO₂ to decompose into NO and O on the MnO₂(110) and the CeO₂(111) supported Mn₂O₄ cluster.